A Novel Method to Produce Silver Foams with Multi-level Porosities

Seksak Asavavisithchai [a], Ekasit Nisaratanaporn [a] and Yuttanant Boonyongmaneerat [b]

[a] Department of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand.
[b] Metallurgy and Materials Science Research Institute (MMRI), Chulalongkorn University, Bangkok, 10330, Thailand.

Author for correspondence; *e-mail: fmtsas@eng.chula.ac.th
**e-mail: yuttanant.b@chula.ac.th

Received: 9 April 2009
Accepted: 20 May 2009.

ABSTRACT

Open-cell silver foams exhibiting a hierarchical pore system have been successfully produced through a novel powder-based replication approach which combines the uses of a space-holder and a chemical reduction process. The architecture of the foams is comprised of struts with high surface area, macropores, and micropores, which are respectively produced through partial reduction of silver salt, removal of the space-holder, and elimination of the remaining silver salt cores.

Keywords: silver, metallic foam, powder technology, porosity, microstructure.

1. INTRODUCTION

Open-cell metallic foams are excellent for functional applications, such as filter, heat exchanger and catalytic support, mostly due to their large penetrable internal surface area. Most production methods of open-cell metallic foams are based on replication process because precision and uniform distribution in pore size and shape, and volume fraction of pores in the foams can be easily controlled [1]. Among several methods, the powder-based technique, which utilises space-holders as pore forming materials, is attractive due to economical production cost and easy handling of materials.

Space-holders are generally classified by their elimination methods as dissolution and evaporation. In the former group, sodium chloride (NaCl), which can be removed after sintering through water leaching, is commonly employed. Zhao and Sun [2-4], for example, developed open-cell Al foams using NaCl as the space-holder and named their technique as the sintering and dissolution process (SDP). The drawback of NaCl uses is that corrosion of metallic matrix might occur if NaCl is not completely removed from foam structure. This in turn can lead to poor mechanical properties of the materials. For the evaporation type, space-holders are removed during sintering of powder green compact [5-9]. Jiang et al [5-7] used carbamide as space holders and obtained more uniform foam structure and better mechanical properties compared with foams made using NaCl. However, carbamide is soft and has a low...
melting point which might not be suitable for foam production of hard and high melting point metals. Recently, Asavavisithchai and Nisaratnaporn [8] used two types of disaccharide, widely known as raw and white refined sugars, as effective dissolution-typed space-holders for their Ag foam production. Although several types of open-cell metallic foams were successfully produced, their cellular structures were mostly restricted to a single porosity level. A viable production of metallic foams with hierarchical pore structure, with pore size ranging from micrometers to sub-micrometers, would provide the possibility of combining attractive features offered by foams of different pore sizes. For example, larger pores exhibit better diffusion of reagents with minimum pore blocking phenomena, while smaller pores are characterised by relatively high surface areas and hence large reaction sites. Metallic foams with such integrated qualities would find great use in many functional and tissue engineering applications [10-12].

The present study describes a production of open-cell Ag foams with multi-level pore structures. The foams were fabricated through a novel technique, which combines the uses of a space-holder, namely white refined sugars, and the chemical reduction process of silver salt. With such technique, silver foams exhibiting macropores and micropores can be obtained.

2. MATERIALS AND METHODS

Silver sulfate (Ag$_2$SO$_4$) powder, with an average particle size of 10 mm, was partially reduced in an aqueous solution which was the mixture of glycerol (C$_3$H$_5$(OH)$_3$) and sodium hydroxide (NaOH) at 120 °C for 1 h. The glycerol and sodium hydroxide were used as reducer and reaction accelerator, respectively. The reaction resulted in a formation of pure Ag covering on the surface of Ag$_2$SO$_4$ cores. The Ag product was obtained as shown in Eqs. (1) and (2). The powder was soaked with ethanol, in order to prevent the occurrence of silver oxide, and was rinsed and finally dried at 110 °C for 1 h in a resistant furnace.

$$3\text{Ag}_2\text{SO}_4 + 6\text{NaOH} \rightarrow 6\text{AgOH} + 3\text{Na}_2\text{SO}_4$$

(1)

$$4\text{AgOH} + \text{C}_3\text{H}_5\text{O}_3 \rightarrow 4\text{Ag} + \text{C}_3\text{H}_6\text{O}_4 + 3\text{H}_2\text{O}$$

(2)

Next, using a rocking mill, the partially-reduced Ag$_2$SO$_4$ powder was mixed with white refined sugar (554 μm) at the proportion of 45(powder):55(sugar) by volume. The mixture of 10 g was uniaxially cold pressed in a 22 mm diameter tool steel die at 600 MPa. To remove the sugar, the green compact was placed in a glass beaker filled with hot water of 95 °C for 1 h, and fresh water was replaced after 30 min. The sample was dried at 110 °C for 3 h before sintering to achieve mechanical integrity of the structure. Sintering of the samples was carried out at 600 °C for 5 h in air. Finally, the remaining Ag$_2$SO$_4$ in the samples was removed in 25% concentration NH$_4$OH for 24 h. The relative foam densities were calculated through the measurement of specimens’ dimensions and weights. The volume fractions of macropores ($V_{mac}$) and micropores ($V_{mic}$) were determined according to Eqs. (3) and (4) below:

$$V_{mac} = \frac{1-V}{1-(m_f - \rho_f V_f)/\rho_2}$$

(3)

$$V_{mic} = (1-V_{mac})(1-V)/\rho_4$$

(4)

where $V$ is volume fraction, $\rho$ density, $m$ foam mass after sintering, and $m_f$ final foam mass. The subscripts 1, 2, 3, and 4 denote partially-reduced Ag, white refine sugar, Ag, and AgSO$_4$, respectively. To prepare foam samples for microstructural examination, the
samples were half-sectioned along the mid-plane using a Buehler Isomet 2000 precision saw. Foam structure was examined using JSM-5800LV scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the morphologies of partially-reduced Ag$_2$SO$_4$ powders and white refined sugar particles. The size of the Ag$_2$SO$_4$ powders is approximately 10 μm. No agglomeration of the powders was observed. The white refined sugars have polygonal shape and smooth surfaces with a mean diameter of about 554 μm. It can be observed that at the surface of partially-reduced Ag$_2$SO$_4$ powders, there present rough Ag sponge layers, which are formed on Ag$_2$SO$_4$ powder cores as a result of the chemical reduction treatment. The formation of the sponge structure is due to a variation of reduction rates across the surface of Ag$_2$SO$_4$ powders. With the reduction parameters employed in the study, the relative volume of Ag to Ag$_2$SO$_4$ is estimated as 77:23.

Figure 1. (a) Morphologies of partially-reduced silver sulfate powders and (b) white refined sugar particles.
Figure 2 presents the microstructure of Ag foam with the total porosity of 65%, comprising ‘macropores’ and ‘micropores’ with volume fraction of 55 and 10, respectively. The relatively large pores are formed after removing the sugar particles, and thus the morphology and pore size are replicated those of sugar particles. The pores are uniformly distributed in the foam and are either directly interconnected between pores or indirectly interconnected via permeable cell walls.

Figure 2. Pores created after removing the white refined sugar space-holders.

Micropores of Ag foam were generated following $\text{Ag}_2\text{SO}_4$ cores’ removal, as depicted in Figure 3. The pores are well interconnected and uniformly distributed throughout the foam structure. The shape of micropores is irregular and the size is approximately 10-20 μm, corresponding to the mean size of $\text{Ag}_2\text{SO}_4$ particles.

Figure 3. Interconnected micropores after elimination of $\text{Ag}_2\text{SO}_4$ core.
Struts of the Ag foam were formed by mechanical and thermal bonding during the compaction and sintering, respectively. It can be observed from Figure 4 that the surface of struts is comprised of polygonal nodules with estimated size of 0.5-3 μm, and the EDS analysis indicated that the chemical compositions of the nodules are highly rich in Ag. The formation of such nodules, which provides struts of high surface areas, may be attributed to the consolidation of the Ag sponge layers.

Figure 4. Morphology of a nodular cell strut created after removing the remaining silver sulfate.

With the combined uses of the space-holder and chemical reduction techniques, Ag foams with hierarchical structures have therefore been obtained. While macropores can be formed through removals of space-holders, micropores and strut nodules can be obtained from a chemical treatment. The novel processing method presented here is unique in that the sizes of macropore and micropore, and degree of roughness of foam struts could be tailored simply by selecting space-holders with a suitable size, and controlling the chemical reduction rate and duration. Particularly, by controlling solution concentration, reducing temperature, and holding time, the relative thickness of Ag sponge layers and Ag2SO4 core could potentially be modified - the relationship between reduction levels of Ag2SO4 and properties of the final foams is a subject of the ongoing research. The foam fabrication technique demonstrated here therefore offers the possibility for a modification of foams’ architectures, which in turn determine the properties and functionality of the materials.

4. CONCLUSIONS
Open-cell silver foams with porosity of 65% exhibiting a multi-level pore structure, with macropores (~500 μm; 55%), micropores (~10 μm; 10%), and nodule structure of foam struts, have been successfully produced through a powder-based replication approach using white refined sugars as a space-holder, combined with the chemical reduction process of silver salt. The silver foams may be suitable for functional applications, such as highly porous supports
in catalytic process for which a large surface area and good transportation of reagents are essential. The novel technique introduced in this work thus serves as an effective route for a production of hierarchical-structured foams with potential of porosity controlling.

5. ACKNOWLEDGEMENT
The authors would like to acknowledge Mr. Assanai Jaipuem for helps with the experiment.

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