Thermochimica Acta 664 (2018) 73–80

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Enhanced CO_2 capture capacity on open-cell Mg foams via humid impregnation with lithium at low temperatures

M. Velasco-Castro, I.A. Figueroa[*], H. Pfeiffer, J.F. Gómez-García

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México (UNAM), Circuito Exterior S/N, Cd. Universitaria, C.P. 04510, Mexico City, Mexico

ARTICLE INFO

Keywords:
Magnesium foams
Lithium
Oxidation
CO_2 capture
Thermogravimetric analysis

ABSTRACT

In the present work, carbon dioxide capture capacity was evaluated after a humid impregnation process performed on the surface of open-cell magnesium (Mg) foams, with an alkaline solution of lithium hydroxide (LiOH). The Mg foams were fabricated by the infiltration casting method, using irregular particles of sodium chloride (NaCl) as space holders. Optical microscopy, helium (He) pycnometry and nitrogen (N_2) adsorption-desorption techniques were used to measure the pore size, density (ρ_{foam}) and specific surface area (A_s), respectively. The microstructural modifications after the impregnation process were analysed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Afterwards, a thermogravimetric analysis was performed to evaluate the CO_2 capture capacity under different water steam (H_2O) conditions. After the H_2O–CO_2 chemisorption process, the carbonated products were identified by the attenuated total reflexion – Fourier transform infrared spectroscopy (ATR-FTIR) technique and then, quantified through a thermal decomposition process. Thermal analysis outcomes showed that H_2O–CO_2 chemisorption capacity of the Mg foams considerably increased after lithium (Li) impregnation. The later as consequence of the lithium oxide (Li_2O) high reactivity with CO_2, and its effect on the thickening of the oxide film layer formed on the surface of the open-cell Mg foams. These results promote the possible use of this kind of cellular material as structured CO_2 captor, proposing a new functional application for metallic foams and giving an alternative solution to the current environmental issues.

1. Introduction

Cellular metals and metallic foams have been used in a number of structural and functional applications [1–5], such as fluid filters, heat exchangers, supports for catalysis and most recently as structured carbon dioxide (CO_2) captors [6]. Because of porosity, these materials have shown an excellent combination in their physical and mechanical properties, for instance, high energy-impact absorption accompanied by a relative low-mass or mainly due to high-strength to light-weight ratio, among other features [1,5]. Recently, Mg foams have not only demonstrated capabilities for several functional purposes like thermal and acoustic insulation [3,4], but also as a promising biomaterial for bone implants [7,8]. However, environmental functions have not been deeply studied. From engineering and ecological points of view, open-cell Mg foams are able of preserving both, functional and structural applications, meanwhile they can also be used as structured CO_2 captors. It has been proved that these type of materials can be successfully applied in the chemisorption of CO_2 [6].

Nowadays, efforts to face up and diminish the current effects of environmental issues related to global warming, have become an imperative global concern [9], and both theoretical and practical research are, constantly, being developed [10–16]. Within all carbon capture and storage technologies, many sorbent materials, i.e. activated carbons, zeolites, organic-inorganic hybrids, hydrotalcite-like compounds, alkali-metal ceramics and calcium oxide, have been mainly studied and proposed as prominent CO_2 captors [10,12,13]. Nevertheless, alkali-metal-based oxides have attracted great interest as a result of their high-adsorption capacity, low-cost and availability [11,14]. Recently, several manuscripts have reported the capture of CO_2 by applying binary compounds of metallic oxides, with at least one alkali-metal in their chemical composition, in a wide range of temperatures [11,14]. Moreover, owing to catalytic activity offered by these type of materials, their application has not been exclusively limited to separate CO_2 from pre-combustion or post-combustion flue gases, but also to perform steam reforming processes, such as CH_4 or CO conversion to CO_2 [17].

It has been reported that chemical and physical modifications performed on different ceramic materials with lithium (Li), either doped or mixed to produce solid solutions, enhance the kinetic factors, promoting a greater chemisorption capacity of CO_2 [18]. It is worthy of

---

[*] Corresponding author.
E-mail address: iafigueroa@unam.mx (I.A. Figueroa).

https://doi.org/10.1016/j.tca.2018.04.009
Received 21 February 2018; Received in revised form 17 April 2018; Accepted 18 April 2018

note that these modifications could reach a high amount of CO_2 capture under dry conditions [19]. On the other hand, several ceramics compounds such as aluminates ($\alpha - Li_5AlO_4$) [20], cuprates (Li_2CuO_2) [21], ferrites ($Li_{1+x}FeO_2$) [22], silicates (Li_8SiO_6) (Li_4SiO_4) [23] and zirconates (Li_2ZrO_3) [24], have been tested under water steam flows and low temperatures (30–80 °C), showing promising results for CO_2 capture. Likewise, it is also reported that addition of alkali-metals (e.g. Li, Na and K) via humid impregnation on different adsorbent materials, such as hydrotalcite-like compounds [25,26] or metallic oxides [27], notably modified their textural properties (e.g. surface area, porosity, particle size, etc.) and therefore, their CO_2 chemical sorption capacities are also influenced and indeed improved.

The key advantages offered by open-cell Mg foams are their excellent mechanical properties, high surface area and interconnected porosity. The latter implies more active surface available for chemical reactions, allowing gases to flow freely throughout the entire porous network. Moreover, these materials might be used in several cycles after a decarbonation process. Hence, the objective of the present work was to study the CO_2 capture capacity on open-cell Mg foams after being impregnated with lithium via humid media (alkaline solution) and subsequently oxidized under certain conditions. The process of CO_2 capture was carried out under different humid conditions and low temperatures.

2. Experimental procedure

2.1. Fabrication of open-cell Mg foams

Open-cell Mg foams were manufactured by the infiltration casting method. This method has been widely applied to produce cellular materials with complete open-porosity [4,8]. Argon (Ar, 99.99%) was used to maintain an inert atmosphere, promoting the infiltration of the molten metal throughout the irregular particles of sodium chloride (NaCl, 99.95%). NaCl particles were sieved and classified in one average size (510–710 μm). Firstly, NaCl particles were deposited inside the crucible to assemble the porous preform, and then Mg ingots (99.5%) were located on top of them. The dimensions of the austenitic stainless-steel 304 cylindrical-chamber are 73 mm of outer diameter, wall thickness of 2.9 mm and a height of 20 cm. Thereafter, the casting process takes place and the Mg load was melted at 750 °C under a constant gas pressure of 50 kPa, for 1 h. Afterwards, the molten metal was infiltrated through the preform using a gas pressure of 1.5 bar for 15 min, and subsequently cooled down at room temperature. After this, a complete solid Mg–NaCl composite was produced, and then the final ingot was machined to obtain several cubic-shaped samples ($\sim 1cm^3$) for the study. With the aim of removing the NaCl particles and obtaining a free-salt metallic foam, the Pourbaix diagram (potential − pH) was considered [28]. Hence, the composite was immersed into an alkaline solution of sodium hydroxide (NaOH, 99.95%, pH = 13) to dissolve the NaCl particles and prevent corrosion by pitting [28]. Because of the pores and dimensions of the cubic-shaped samples (with shallow relative depth), the implementation of ultrasonic vibrations was enough to increase the dissolution rate and release gas bubbles entrapped into the porous network, avoiding overexposure to the alkaline solution that might lead to detrimental effects, such as corrosion.

From the micrographs obtained by optical microscopy, at least 100 measurements were taken to estimate the average pore size. The last mentioned was achieved by using an image processing software and the line intercept sampling. An Ultrapyc-1200e pycnometer for solids (pulse method and helium atmosphere) was used to determine the density of the open-cell Mg foams (ρ_{Mg}), and subsequently the percentage of porosity (% Pr) was calculated by means of the relative density ($\rho_{Relative}$). BET specific surface area was determined by N_2 adsorption-desorption experiments, which were performed on a Bel-Japan Minisorp II equipment at 77 K using a multipoint technique. The samples were degasified at 80 °C for 24 h under vacuum, prior to the corresponding analysis.

2.2. Impregnation and superficial oxidation of the open-cell Mg foams

An alkaline solution of lithium hydroxide (LiOH) with pH = 13 was prepared. This solution was used as lithium-ion precursor, and to prevent possible corrosion effects on the surface as already explained. The cubic-shaped samples were immersed into the LiOH solution for 30 min. Then, the impregnated samples were dried off, by a superficial oxidation process, in a tubular furnace using an oxygen (O_2, 99.99%) flow of 40 mL/min at 500 °C for 1 h. With the aim of conserving the structural integrity of an open-cell Mg foam, a thin oxide layer must be formed after the superficial oxidation process. Therefore, these experimental conditions (500 °C for 1 h) were previously established to form an oxide layer of 6 (±2) microns on the cell walls of an open-cell Mg foam [6].

With the aim of identifying the crystal phases formed during the oxidation stage, and after the CO_2 capture process; oxidized samples and carbonated products were characterized by X-ray diffraction (XRD), using a diffractometer Bruker AXS-D8 Advance, coupled to a copper (Cu) anode X-ray tube ($\lambda_{Cu-K\alpha_1} = 0.15406nm$) working at 30 kV and 30 mA, with a step size of 0.02° (2θ) and step time of 12 s in the range from 30° to 80°. X-ray patterns were identified by the corresponding Joint Committee Powder Diffraction Standards (JCPDS) files. Furthermore, the microstructural morphology of the samples before and after the CO_2 capture process was analysed with a scanning electron microscope JEOL JMS-7600F. Additionally, all samples, before and after the CO_2 capture process, were analysed by Fourier transform infrared (FTIR) spectroscopy using the attenuated total reflexion (ATR) module on a spectrometer Alpha-Platinum (Bruker).

2.3. CO_2 capture experiments

Dynamic and isothermal experiments were performed using a humidity-controlled thermo-balance TA instrument model Q5000SA. Experiments were carried out using distilled water, and CO_2 (Praxair, grade 3.0) as carrier gas with a flow rate of 60 mL/min. Dynamic H_2O–CO_2 sorption-desorption isothermal experiments were performed at different temperatures (40 and 60 °C) while varying the relative humidity (RH) from 0 to 80% and then from 80 to 0% at a rate of 0.5% per minute. On the other hand, isothermal measurements were performed at specific temperatures (40 and 60 °C) and different values of RH (30, 50 and 70%) for each temperature condition. Thereafter, XRD, SEM, and FTIR techniques were used to characterize the samples and identify the carbonated products. With the aim of quantifying the amount of H_2O–CO_2 sorbed on the surface, a thermogravimetric analysis (TGA) was performed under nitrogen (N_2, Praxair grade 4.8) atmosphere, using a thermo-balance TA instrument model SDT600. The decomposition process was carried out within a temperature range of 30–450 °C, with a heating rate of 5 °C per minute.

3. Results and discussion

3.1. Porous structure

Fig. 1 shows the micrograph that corresponds to the cellular network of an open-cell Mg foam manufactured by the infiltration casting method with an average pore size of 710 ± 30 μm (μm), using irregular particles of NaCl as space holders. From this image, a uniform pore distribution and complete interconnected porosity are corroborated through the whole volume of the structured material. Moreover, regarding the size and shape of the porous network, both aspects are equivalent to those particles used as space holders. As mentioned before, these features are appropriate for the objectives of the present work, since gases will be allowed to flow freely throughout the entire porous network. On continuing the structural-physical analysis, the relative density ($\rho_{Relative}$) was determined with the following expression: