LEAD AND LEAD ALLOYS FOAMS PRODUCTION

Girolamo Costanza[1)*], *Maria Elisa Tata*[2)]
[1)]*University of Rome "Tor Vergata" Industrial Engineering Department, Rome, Italy*
[2)] *University of Rome "Tor Vergata" Civil Engineering and Computer Science Department, Rome, Italy*

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[*]*Corresponding author: costanza@ing.uniroma2.it:, Tel.: +39 06 72597185, Industrial Engineering Department, University "Tor Vergata", Via del Politecnico, 1 – 00133 Rome Italy*

Abstract

Low-cost techniques for the manufacturing of lead and lead-alloys foams have been investigated in this work. In particular the "sintering and dissolution process" (SDP) and "replication process" (RP) have been focused and discussed. The effects of some process parameters have been investigated too: powder compacting pressure, composition of the base metal, granulometry, sintering time and temperature. Spherical urea and NaCl have been employed in the SDP method. In the replication process the melt viscosity has been found the main parameter. Furthermore melt infiltration in the NaCl particles has been found much easier if external pressure is applied. Lead recovery and recycling of exhaust batteries into foam-based electrodes has been examined too with a novel method for the direct conversion of Pb scrap into lead foam.

Keywords: Metal foam, manufacturing, electrodes, properties

1 Introduction

Cellular materials, of great interest for many industrial applications, can be produced by several processing routes [1]. One of the most common methods, developed at the Fraunhofer Institute of Bremen, is based on Powder Metallurgy (PM) [2]. It requires base metal powders, blowing agent and the addition of ceramic particles for modifying melt viscosity and stabilizing liquid metal foam. Many parameters affect the foaming process. In previous works [3-6] the powder mix composition effects have been analysed and discussed. Up to now the scientific community has focused the attention on Al foams but a lot of other metals and alloys can be foamed as well. This work deals with lead and its alloys foams. Some aspects regarding Pb foamability are present in literature. For example in papers [7-9] lead foams are suggested to be used as light-weight electrodes in lead-acid batteries. In [7] Irretier and Banhart analysed different lead powders (twelve) from many manufacturers and the powder method has been adopted as production process. Negative drawbacks have been identified: high powders cost, long mixing time (30 min.), hot pressing for the precursor production (250 °C and 110 MPa for 20 min.), hot extrusion (275 °C after 2 hours of conditioning time) and finally foaming with a furnace temperature in the range 350-550 °C. For these reasons the proposed process by Irretier and Banhart is difficult to apply as an alternative to the traditional method with grids and paste usually employed for the production of standard lead-acid batteries electrodes. Too complex and expensive also the method suggested by Dai et al. [8-9]: despite the performance improvement during battery discharge, lead foam negative grids were produced by Pb alloy electrodeposition on a Cu substrate with negative consequences also on costs.

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Two techniques are proposed in this work for the production of lead foam: SDP (sintering and dissolution process) [10] and RP (replication process) [11]. Both methods have been analysed and suitable modified in order to manufacture low cost lead foams. The main objective is the definition of a production method which could be competing with the standard one usually employed by batteries manufacturer. The possibility to produce foam-based lead electrodes from waste batteries is discussed too and an experimental battery has been prepared with lead-foam electrodes. Great porosity size is available at the moment but further efforts for the improvements of porosity are actually underway.

2 Materials and methods

Two techniques have been employed in this work for the production of lead foam: SDP (sintering and dissolution process) [10] and RP (replication process) [11]. The attention has been focused on the following main objectives: homogeneous porosity distribution inside the metal, easy filler removal, ability to produce manifold geometries and at last acceptable mechanical strength. The SDP technique has been adopted and suitable modified starting from both commercial lead powder (200 mesh) and scrap derived from the negative electrodes of junk batteries. As filler agents both urea and NaCl have been employed. The choice was driven not only by the easy dissolution process (water at 70 °C is enough) but also by the low cost. Before compaction, Pb powders and filler have been mixed to obtain a uniform distribution of both components. After mixing the uniaxial cold compaction has been performed, applying 5 tons as maximum load on a cross section of diameter 15 mm. The successive step of this process has been sintering. Many experiments have been performed and an optimal temperature range has been identified (200-250 °C). Finally the obtained precursor has been successively washed in hot water (70 °C) in order to remove the filler (urea or NaCl).

In alternative, the replication process has been adopted with the main goal of employing bulk Pb and its alloys rather than expensive powders. Reference [11] describes the base process, suitable modified for the different base material and experimental conditions. In this case lead and its alloys melting occur inside a small furnace or applying flame on the external side of the crucible made of copper, stainless steel or aluminium. The last one has been filled with a mix of coarse lead particles and NaCl particles, heated up above lead melting point and finally external pressure has been applied by a suitable piston. Thanks to the applied pressure, melt infiltration has been easier. Further effects of applied pressure under solidification of metals have been described in previous work [12]. Finally for the two lead electrodes production, to be employed for the set-up of the first experimental battery, a rectangular cross-section crucible has been adopted. The dimensions of the crucible have been 13 mm X 27 mm, height 70 mm.

3 Experimental results

The main experimental results are reported in this section. Both SDP and RP methods have been analysed and suitable modified according to the new experimental conditions. Many attempts have been performed, employing lead powder, waste battery powder and grid as base metal, while urea and NaCl as filler agent have been used. Further experimental details are reported in the following.

3.1 SDP method: Pb powder and urea

In order to manufacture lead foam starting from Pb powders many experiments have been carried out. The two fundamental steps (washing and sintering) of the SDP method have been alternatively performed on the precursor. If it is washed before and then sintered, precursor is too brittle and can easily break. If dissolution is performed after sintering, residual urea has been found on the foam surface and it is quite difficult to be removed also after long treatments in hot water. However other authors [7] employed powder method for producing lead foams. Different blowing agents have been tested (hydrides and carbonate) and some commercial powders. In many cases the results were disappointing. In fact the powder method is not the best way to manufacture Pb-foam electrodes because powders are too expensive, pollutant and it is more difficult to control the final porosity.

3.2 SDP method: waste battery powders and NaCl

Powders obtained by grinding waste paste battery have been mixed with NaCl. The precursor (diameter 15 mm) has been produced by cold uniaxial pressing (5 tons) of the mixture in a mould. The optimal sintering temperature and time (250 °C and 30 minutes) have been defined after many experiments. Finally NaCl particles have been dissolved in hot water (70 °C) for 30 minutes. One of the best results obtained with this technique is shown in **Fig. 1**. Pores morphology is far from an optimal solution, in particular it appears inhomogeneous, irregular and too large sized. For these reasons the next step has been to produce Pb foams by adding urea (1.19 mm average size).

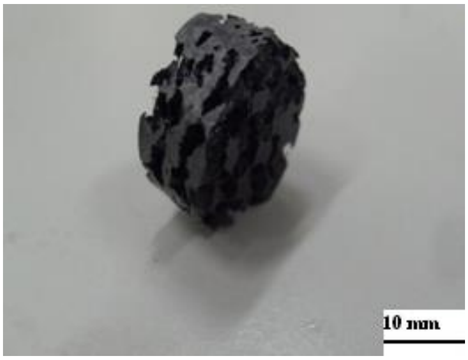

Fig. 1 Lead foam produced with SDP method from waste paste of a battery

3.3 SDP method: waste battery powder and urea

The encouraging results from the previous tests suggested changing the filler: urea instead of NaCl. Despite the precursor, produced with the same experimental procedure previously described, appeared uniform and compact, it broke during washing in hot water.

3.4 RP: Pb granulated and NaCl, Pb-Sn (60-40) and NaCl

Pb melting is fundamental in the replication process. NaCl is adopted as space holder and successively removed in hot water after lead solidification. Nevertheless pure lead fluidity does not allow small porosity size. An example is shown in **Fig. 2**.

For this reason some changes have been made to the process. Fluidity must be improved, for example employing Pb alloy as Pb-Sn (60-40) (**Fig. 3**). An alternative method could be pressure application on the melt through a piston in order to promote the infiltration between the filler particles.

Fig. 2 Lead foam produced by RP process employing coarse NaCl as filler

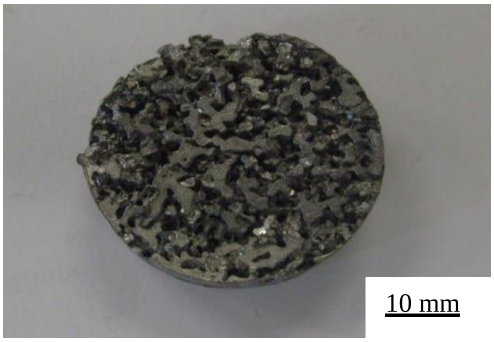

Fig. 3 Pb-Sn (60-40) foam produced by RP process employing coarse NaCl as filler

3.5 RP: Pb-Sn-Sb alloy (grids) and NaCl

As good properties in terms of melt fluidity have been found in Pb-Sn-Sb alloy, employed for the production of grids in lead-acid batteries, it has been decided to make an attempt and use this material as base metal for foam production. The mixture (50-50 vol. %) was prepared with NaCl (average diameter 1 mm) and small lead alloys fragments derived from grids of junk batteries. Alloy melting has been performed by heating the external surface of the crucible. A small pressure has been applied through a piston, after melting, on the top of the liquid metal for optimal infiltration. After solidification NaCl has been removed in hot water. Circular and rectangular cross-section samples (**Fig. 4 a**) have been manufactured. The last ones (density 3 g/cm^3) have been employed as electrodes for the assembly and testing of a prototype battery (**Fig. 4 b**).

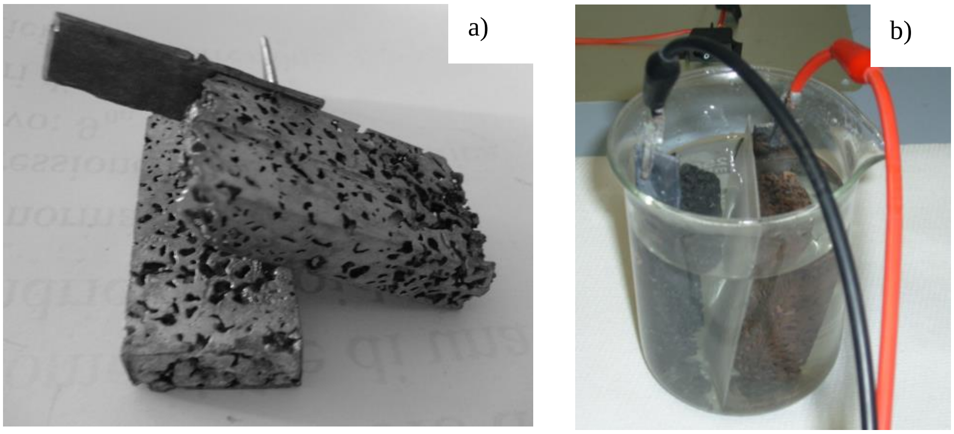

Fig. 4 **a)** Rectangular cross-section lead alloy foams manufactured starting from grids of junk batteries. **b)** The 2V lead-acid cell with electrode foam, charged and discharged.

3.6 Preparation of the experimental battery

Manufacturing of light electrodes for high-efficient lead-acid batteries could be an important challenge, not only for starters but also for traction accumulators in automotive applications.

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References [8, 9] illustrate some electrode production processes based on electrodeposition of Pb on a copper foam substrate. However, electrodeposition is a low-speed process and is difficult to be carried out at low cost in the industrial production. In highly industrialized countries severe regulations are bringing to the production, utilization, collection and recycling of most of the chemical power sources under control [13]. Lead recycling main process employed is the pyro metallurgical process in a rotary furnace [14].

The process suggested in this paper is extremely easy and cheap. It exploits waste grids from batteries and allows the direct conversion of the waste material into new electrodes. The specific surface area is an important parameter for lead foam material. The higher the specific surface area, the higher the efficiency of the active material. A detailed study on the correlation between pores morphology and powder mix composition (for Al foam) is the main goal of a previous paper [3].

After electrodes manufacturing, as described in a previous section, a small-scale test has been performed: a 2V lead-acid cell employing commercial sulfuric acid (31%) was charged and discharged (**Fig. 4 b**). After 4 hours of charge (first cycle) the battery has shown a voltage of 2,2 V. After charging, a small lamp (about 3 W) has been turned on by the battery for 30 minutes. At the moment it is just a qualitative analysis of the potentiality of the new production method. In the future further tests will be performed to quantify the charge-discharge performance of the battery. New foam-electrodes will be manufactured varying the process parameters as porosity, sintering time and temperature, compaction conditions and filler removal.

4 Discussion and conclusion

To produce a high-quality and small-porosity foam the process parameters must be chosen carefully. Fundamental is an appropriate selection of the powders or particles employed, alloy composition, compaction conditions, sintering temperature and time, filler removal method etc.

In the following the most remarkable results of the research are reported. Lead and lead alloy foams can be manufactured modifying the standard sintering and dissolution process or the replication process well known for Al alloys. At the moment uniform foams with density of 3 g/cm^3 have been produced. Lower density and higher amount of porosity can be reached with the same technique modifying the process parameters. Foam lead-electrodes have been manufactured by replication process starting from waste grids of junk batteries. Such electrodes have been assembled and tested with a charge/discharge cycle as lead-acid battery. Actual porosity size is not optimized for the battery efficiency improvement and weight reduction, so further efforts must be focused on the production of low porosity lead-alloy foams. Nevertheless these are the main results of a preliminary investigation. Lead-foam porosity must be reduced at least 2 degrees of magnitude while the effect of lead oxides and sulphate on the battery efficiency must be evaluated too.

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