Renewable Energy xxx (2016) 1–10

Contents lists available at ScienceDirect

Renewable Energy

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

Nanostructured metal hydride – Polymer composite as fixed bed for sorption technologies. Advantages of an innovative combined approach by high-energy ball milling and extrusion techniques

Marzia Pentimalli [a, *], Enrico Imperi [b], Alessandro Zaccagnini [b, c], Franco Padella [a]

[a] ENEA – Italian National Agency for Energy, New Technologies and Sustainable Economic Development, Casaccia Research Centre, Via Anguillarese 301, 00123 Rome, Italy
[b] LABOR s.r.l. – Industrial Research Laboratory, Via Giacomo Peroni 386, 00131 Rome, Italy
[c] Department of Industrial Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form
26 July 2016
Accepted 29 July 2016
Available online xxx

Keywords:
Metal hydride
Polymeric matrix
Extrusion
Ball milling
Sorption
Heat pump
Waste heat recovery

ABSTRACT

Different metal alloys can react highly exothermically and reversibly with hydrogen to form metal hydrides. Based on these reactions several application have been developed, e.g. in fuel cell, in storage for hydrogen gas and in sorption heat pumps. By exploiting the thermodynamical properties of some metal hydriding alloys, cooling energy can be generated by using renewable, sustainable and/or disposable energy sources. However, hydriding alloys show some limitations in their behaviour mainly regarding their intrinsic low thermal conductivity and mechanical stability during the hydriding process. A proper management of these issues is required in practical applications in particular when the metal hydrides have to be stably packed as fixed beds with good mechanical stability, high thermal conductivity, fast kinetics, reproducibility, durability.

In this work a composite material containing a high metal fraction is obtained by an innovative bulk and low cost processing approach by combining high-energy ball milling and extrusion techniques. The methodology is presented and the characterization of a representative $LaNi_5$-type based composite is given. The developed composites were used as fixed beds in the implementation of a Metal Hydride Cooling System. Finally, the system was integrated into a refrigerated transportation vehicle, currently under testing. Some results are reported coming from a preliminary test campaign.

1. Introduction

Every metal hydride-based device should contain the hydriding metals in form of powder to increase the active surface. Also, the repeated hydrogen loading–unloading cycles induce further pulverization of the metal particles due to the large volume mismatch between the hydride and the metal phases [1,2]. Management of free metal powder in fixed beds is required, avoiding the negative effects possibly deriving by powder material transportation due to the hydrogen flux throughout the beds.

Moreover, as the chemical interaction of hydrogen with a metal involves heat exchanges (metal hydride formation is exothermic and H_2 release from the metal-hydrogen compound is endothermic), a proper heat management throughout the material's bed is also required to optimize the thermal conductivity of the material so that heat enters and leaves the material as quickly as possible with beneficial effects in maintaining high adsorption/desorption rates. Besides to the possibility of a proper designing of the fixed beds (for example by adding fins that help with heat transfer), various techniques have been proposed to improve the overall material mechanical stability and thermal conductivity such as compaction of porous metallic matrix, microencapsulated metal hydride compacts, insertion of aluminium foam, integration of copper wire nets, and so on [3–9].

We previously demonstrated [10,11] that the physical–chemical characteristics of Acrylonitrile Butadiene Styrene (ABS) copolymer results suitable for using as embedding matrix for hydrogen storage materials. In facts, in comparison with other well-crystallized polymeric material, the ABS does not show significant gas barrier behaviour, the diffusion processes being favoured by the disordered physical conformation of its polymeric chains. In addition, the presence of the rubber component is able to easily compensate the

* Corresponding author.
E-mail address: marzia.pentimalli@enea.it (M. Pentimalli).

http://dx.doi.org/10.1016/j.renene.2016.07.074
0960-1481/

volumetric variations exhibited by the alloy phase during H_2 loading and unloading cycling inside the embedding polymeric matrix.

We also reported [12,13] about the possibility of enhancing the overall thermal conductivity of metal hydrides embedded in a silica matrix by the addition of an amount of conductive filler. It was assessed that: i) the method of loading the matrix with a conductive filler is suitable to enhance the overall thermal conductivity; ii) the filler in form of graphite powder results much efficient with respect to the flakes; iii) the addition of 10% V of filler is sufficient to obtain an increase of one order of magnitude of the thermal conductivity of the composite with respect of the value of the starting metal hydride (typically for $LaNi_5$, $\lambda \approx 0.1$ W/mK) with minimal expected structural modification with respect to a reference sample.

Clearly, the use of a unique and simple material processing approach to address both the issues of powder dispersion risks and low thermal conductivity would result practically advantageous. In addition, when considerable amounts of active metal phases are required for implementing practical devices, the material processing has to necessarily be based on low cost and easily scalable techniques.

Here, at the aim to develop a metal hydride-matrix composite able to embed the hydriding particles with minimal detrimental effects on the end performances and having enhanced thermal conductivity, we propose an innovative material processing approach based on a combination of ball milling and extrusion techniques.

Based on the previous experience, the ABS copolymer is chosen as matrix also due to its rheological and thermal properties that make it easily workable by extrusion and, not last, for its wide availability and low cost. Due to the extremely challenging required composition for the final composite material (low polymer content), an accurate tuning of the processing technologies was necessary and crucial mainly to overcome the homogeneity concerns deriving from the enormous difference in the densities of the polymeric matrix (about 1 g/cm^3), the graphitic filler (about 2 g/cm^3) and the metal alloy (more than 8 g/cm^3) counterparts, respectively.

In this work we used various AB5 particles alloys as active materials to be embedded in an ABS matrix containing graphite powder as filler. The chemical-physical and functional characterizations of the obtained composite samples are reported.

Some of the developed composites were used as active materials assembled in fixed beds to implement an innovative metal hydride-based heat pump system. Some preliminary results as obtained from the testing of the heat pump system are also related about.

2. Materials and methods

2.1. The metal hydride

In this work we used different $LaNi_5$-type metal hydride alloys (particles size 1 ÷ 100 μm diameter) supplied by Saes Getters. The alloys were preliminarily tested to check their stability with respect the mechanical action in air. For the purpose some portions were milling treated in a stainless steel cylindrical vial (60 cm^3 volume) by means of a SPEX 8000 M High Energy Miller apparatus. Samples aliquots were milled with stainless steel balls (10 mm diameter) with a constant powder to balls ratio of 1:10 (typically, 4 g of alloy and 40 g of milling media). Samples were prepared at 15, 30, 60, 90 and 120 min milling times, respectively. The metal samples to be used as particulate dispersion into the composite were directly obtained in the Zoz Simoloyer CM02, preliminarily to the successive blending action (see in the following), by milling about 1 kg of the starting at 1000 rpm for 10 min (2 L vial, stainless steel balls, 5 mm diameter, about 1:12 powder to balls ratio).

2.2. The polymeric matrix

The ABS Sinkral® used in this work as embedding matrix was supplied by Versalis Spa coming from an industrial production process of mass polymerization. The resulting polymer shows good strength, toughness, impact resistance and dimensional stability properties. Samples were supplied in form of spherical pellets and reduced in powder particles by using centrifugal milling technique (Fritsch Pulverizette 14 high-speed rotor mill) after their embrittlement in liquid nitrogen. The centrifugal action was carried out at 15000 rpm with a 0.5 mm diameter sieve.

2.3. The conductive filler

A low cost commercial graphite powder (99% purity, <2 mm particle diameter, ≈2 €/kg Aldrich) was used as conductive filler of the polymeric matrix. A loading amount of 10% in volume of fresh, as received, graphite powder was added to the metal phase and blended by means of the high-energy ball milling treatment described here below.

2.4. Blending of the metal-matrix-filler mixture by ball milling

The metal-matrix-filler mixtures containing the three components in 45/45/10 vol ratios were blended by means of high-energy ball milling using a Zoz Simoloyer CM02 apparatus. The vial (2 L volume) was filled with the material and the milling media (stainless steel balls, 5 mm diameter) with a constant powder to balls ratio of 1:10. The treatment consisted in a preliminary milling (15 min at 1000 rpm) of the metal alloy-graphite mixture followed by a successive milling for (5 min at 1000 rpm) after the addition of the polymeric fraction. At the end the blended batch (about 1.2 kg) was recovered from the vial and separated from the ball media trough a 3 mm diameter sieve.

2.5. Extrusion of the metal-matrix-filler blend

The metal-matrix-filler blends as obtained by the above described ball milling treatment were extruded by using a bench top Compounder ZK 25T x 18/24 D by Dr. Collin GmbH. The apparatus is equipped with two counter-rotating twin screws, a volumetric feeding system, an in-line water bath to cool the extruded wire followed by a pelletizer to reduce the wire in cylindrical pellets. The process was carried on at 67 rpm tween screws speed. The thermal profile of the apparatus was set at 110/130/150/200/220 °C for the five zones, respectively. The final composite was obtained in form of wire and cut in form of cylindrical pellets (≈2 mm diameter per ≈3 mm height) by means of the pelletizer.

2.6. Chemical physical and functional characterization

X-ray diffraction analyses were carried on the $LaNi_5$-type alloy for the as received, milled and final composite samples. The diffraction patterns were obtained by using a X-RED 3000 instrument by Italstructure equipped with a Fe emitting tube, monochromator on the primary beam and a simultaneous INEL detector with 4097 channels corresponding to 120° of simultaneous data acquisition. Comparing the experimental data with the standard cards of the JCPDS-ICDD 1999 database phase identification was assessed.

The *morphological features* of the samples were observed by high resolution scanning electron microscopy analyses using a FE-SEM LEO 1530 microscope.

Please cite this article in press as: M. Pentimalli, et al., Nanostructured metal hydride – Polymer composite as fixed bed for sorption technologies. Advantages of an innovative combined approach by high-energy ball milling and extrusion techniques, Renewable Energy (2016), http://dx.doi.org/10.1016/j.renene.2016.07.074