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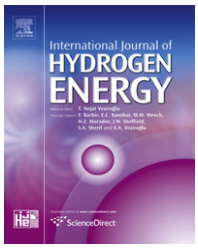

Development of nanostructured Mg_2Ni alloys for hydrogen storage applications

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ABSTRACT

The Mechanically Activated Self-propagating High temperature Synthesis (MASHS) has been employed to obtain nanostructured Mg_2Ni alloys. MASHS process has been further improved by controlling the electrical parameter measurements during the combustion reaction under the thermal explosion mode. The samples were hydrogenated at 20 bar and 300 °C by means of a Pressflow Gas Controller while the dehydrogenation was conducted in a Differential Scanning Calorimetry (DSC) equipped with an H_2 detector of the purged gas. Nanostructured Mg_2Ni demonstrated hydrogen storage capacity around 3.5 wt%. The desorption temperature was about 250 °C at 3 °C/min. The activation energy for dehydrogenation, calculated by the Kissinger method, was about 100 kJ/mol.

1. Introduction

Metal hydrides based on Mg–Ni alloys are very promising materials for hydrogen storage applications since they have high storage density, light weight and reversible hydriding behavior. On the contrary, these alloys present slow hydrogen sorption kinetics and high absorption/desorption temperatures. Some solutions have been proposed for enhancing these technological issues, such as the formation of non-stoichiometric compounds [1], the production of nanostructured alloys [2], the addition of alloying elements [3–5] or the use of oxides additives [6].

Several methods of synthesis have been widely employed for Mg_2Ni production. Among such methods, the following can be mentioned: conventional melting [7], mechanical alloying [8,9], reactive milling [10], melt-spinning [11] and combustion synthesis [12].

Recently, an alternative method for the preparation of nanostructured Mg_2Ni has been proposed [13]. It is based on the combination of a mechanical alloying and a combustion synthesis processes and it is known as Mechanically Activated Self-propagating High temperature Synthesis (MASHS). This process exploits the exothermicity between the precursor powders to cause the reaction thanks to application of an external heat source. In this way, an ignition is provoked and then a self-sustained reaction takes place in the sample's volume, spontaneously converting the reactants into combustion products. The very high combustion temperature that is reached in a short time explains the current use of the term "thermal explosion". In particular, the Mg–Ni system needs a previous mechanical activation since it has a low exothermicity, inhibiting the ignition and propagation of the reaction. Therefore, the mechanical activation step is used

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to increase the reactivity of precursor materials before the reaction.

In this work, innovation of the process control was successfully achieved with reference to hydrogen sorption properties of nanocrystalline Mg_2Ni. The thermal behavior of hydrogen desorption from hydrogenated powders is also reported.

2. Materials and methods

The precursor materials were magnesium (Aldrich, −50 mesh, purity >99%) and nickel (Sigma Aldrich, <3 μm, 99.7% assay) powders. Magnesium in excess was added to prevent the Mg losses during the reaction, so that the nominal composition used was $Mg_{2.25}Ni$.

Mechanical activation of reactant powders was performed in a planetary ball milling equipment (Fritsch P5) under Ar atmosphere for 24 h. The ball to powder-weight ratio was 10:1. Afterward, cylindrical pellets with 10 mm of diameter were obtained by cold pressing in a stainless steel die. The pellet was placed in a graphite die between two graphite punches. Then, the SHS process under the thermal explosion mode was conducted by means of an electric current flow for 90 s through the pellet and the die, together with a mechanical load (2 MPa) through the die plungers. Subsequently, the electric source was switched off, allowing the sample to be naturally cooled down to room temperature. All experiments were done in air, so that a tiny amount of oxide was expected.

The hydrogen absorption tests were conducted in a High Pressure Autoclave connected with Büchi Pressflow Gas Controller bpc at 20 bar and 300 °C for 15 min. Two complete hydriding cycles were carried out. The samples were tested in pellet form, as they resulted from the MASHS process, since some advantages can be obtained, such as the maximization of their weight/volume ratio and the increase of their resistance to oxidation. Results of hydrogenation are reported as arbitrary units, because of the lack of a proper calibration of the reaction chamber.

Dehydrogenation of previously hydrogenated Mg–Ni samples was evaluated using a Differential Scanning Calorimetry (DSC) apparatus Perkin Elmer DSC7 equipped with an H_2 detector of the purged gas, under argon flow at different heating rates (3, 5, 10, 15 and 30 °C/min) from 55 °C to 500 °C.

Microstructural characterization was done by means of a LEO SUPRA 35 Field Emission Scanning Electron Microscopy (FESEM) and a JEM Jeol2100 Transmission Electron Microscopy (TEM). Both instruments were equipped with EDS/EDAX microprobe. Samples were characterized by X-ray diffraction (XRD) on a X'Pert Philips in the 2θ range between 10° and 80°, radiation Cu Kα with $\lambda = 0.154060$ nm and a counting time of 1 s per 0.02° step. The Rietveld refinement of the XRD patterns was employed for the determination of structural and microstructural parameters by means of the Maud program [14]. In addition, the hydrogenated samples were characterized with the same diffractometer using the non-ambient chamber. The analyses were carried out as a function of time every 50 °C, starting from 100 °C up to 500 °C in Ar atmosphere. The heating rate used was 5 °C/min and the holding time for stabilization was 10 min for every measurement performed.

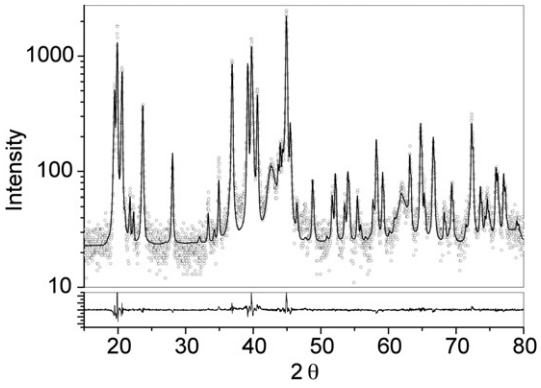

Fig. 1 – XRD pattern of Mg/Ni sample obtained by MASHS technique. Experimental (points) and Rietveld refined (line) patterns are reported, together with their difference (bottom).

3. Results and discussion

Fig. 1 shows the X-ray patterns, both experimental and calculated by the Rietveld method, of the sample with nominal composition equal to $Mg_{2.25}Ni$ produced by MASHS technique. The results of the analysis are reported in Table 1. The refinement revealed traces of unreacted pure metals, suggesting an incomplete transformation to the final products, constituted by Mg_2Ni as main phase, MgO in significant quantity (19 wt%) and a small amount of $MgNi_2$ (about 3 wt%). In this case, the Mg excess in the starting mixture induced the formation of MgO, since the thermal explosion reaction was performed in air, in quantity exceeding the starting content. The remaining excess of Ni reacted with magnesium forming the $MgNi_2$ intermetallic compound.

The microstructure of the sample synthesized by MASHS process is reported in Fig. 2. The TEM image (Fig. 2a) reveals randomly distributed nanocrystals. The distance between the lattice planes was measured as 1.85 and 2.00 Å, corresponding to the hkl Miller index (115) and (203), respectively, of Mg_2Ni, in accordance with the JCPDS card no. 75-1249. The dimension of the Mg_2Ni crystallites can be evaluated varying between 5 and 10 nm. From the FESEM image (Fig. 2b), a distribution of the particle size can be observed, ranging from about 10 nm up to about 50 nm can be observed. By correlating the morphological analysis and the XRD results, it is possible to conclude that the Mg_2Ni alloy synthesized by MASHS showed a wide distribution of the crystallite size, varying from few nanometers up

Table 1 – Rietveld refinement results for as-prepared material. R% = 14. Small contributions from parent Ni and Mg are also present.

	Mg_2Ni	MgO	$MgNi_2$
a_0 (Å)	5.217	4.222	4.840
c_0 (Å)	13.282	–	15.832
Cryst. size (nm)	160	15	120
Microstrain	3.9×10^{-4}	6.7×10^{-3}	2.0×10^{-4}
wt%	77	19	3